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## Full communication

# Vanadium phosphide–phosphorus composite as a high-capacity negative electrode for sodium secondary batteries using an ionic liquid electrolyte

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## ABSTRACT

A vanadium phosphide–phosphorus composite,  $V_4P_7/5P$ , is investigated as a negative electrode for sodium-ion batteries using the ionic liquid,  $Na[FSA]-[C_3C_1pyrr][FSA]$  ( $FSA = \text{bis}(\text{fluorosulfonyl})\text{amide anion}$  and  $C_3C_1pyrr = N\text{-methyl-}N\text{-propylpyrrolidinium cation}$ ), as the electrolyte. Analyses of the X-ray diffraction pattern, X-ray photoelectron spectra, and transmission electron microscopy images revealed that the  $V_4P_7/5P$  composite prepared by high-energy ball-milling is composed of a  $V_4P_7$  crystalline phase and an amorphous phosphorus phase. This composite exhibits a high reversible discharge capacity of  $738 \text{ mAh g}^{-1}$  with a reasonably high initial coulombic efficiency of 85.9% at 363 K, even in the absence of carbon materials. The emergence of  $Na_3P$  peaks in the ex situ XRD pattern after full charging indicated sodiation of the excess amorphous phosphorus present in the composite. The peaks corresponding to  $V_4P_7$  remained intact and desodiation of  $Na_3P$  after full discharge was also evident from the XRD pattern. The cyclability was higher in the ionic liquid electrolyte than in an organic electrolyte owing to the formation of a more efficient interfacial layer in the former.

## 1. Introduction

Sodium-ion batteries (SIBs) are believed to be a suitable technology for high-energy-density and low-cost stationary energy storage systems, owing to their low standard electrode potential ( $-2.71$  vs standard hydrogen electrode), abundance of sodium resources, and use of an aluminum current collector [1–4]. Recently, phosphorus-based compounds are being widely used as negative electrodes in SIBs owing to the high theoretical capacity ( $\sim 2596 \text{ mAh g}^{-1}$ ) of elemental phosphorus, due to the formation of  $Na_3P$  after sodiation [5]. However, owing to the low electrical conductivity of phosphorus ( $\sim 10^{-14} \text{ S cm}^{-1}$ ) and large change in volume during sodiation and desodiation, severe capacity fade is often observed. The difficulties arising from the large volume change can be attenuated by using metal phosphides, including  $Cu_3P$ ,  $CuP_2$ ,  $FeP_4$ , and  $Sn_4P_3$ , which form a conductive matrix of metal after sodiation [6–9] and by limiting the desodiation of phosphorus which was reported recently in the case of  $Sn_4P_3$  [10]. However, the cyclability and rate capability are still limited. Although the introduction of carbon to the metal phosphide improves the rate capability and cycle performance [11,12], the tap density of the material decreases because of the low density of carbon,

while the first-cycle coulombic efficiency reduced owing to the side reactions arising from the large surface area. Hence, a metal phosphide with a buffer, rather than carbon, can give a new direction for fabricating negative electrodes for SIBs.

The  $P\text{-TiP}_2\text{-C}$  composite prepared by ball-milling showed excellent cyclability and rate performance as a negative electrode for both lithium-ion batteries (LIBs) and SIBs [13].  $TiP_2$  could buffer against the large volume change during the sodiation/desodiation, owing to its structural stability and inactivity toward sodiation/desodiation. Vanadium phosphides ( $VP$ ,  $V_4P_7$ , and  $VP_2$ ) have been already investigated as negative electrodes for LIBs [14,15];  $VP$  showed a moderate capacity with good cyclability owing to a very low volume change during cycling, while  $VP_2$  exhibited high capacity but poor cyclability. The characteristics of  $V_4P_7$  was intermediate between the other two phosphides, and it exhibited high capacity as well as good cyclability and rate capacity [16]. X-ray diffraction (XRD) and X-ray absorption (XAS) analyses suggest that all the aforementioned vanadium phosphides function according to an insertion mechanism. A recent study for  $V_4P_7$  for SIBs showed excellent cyclability and rate performance [17]. This may be related to the relatively low resistivity of  $V_4P_7$  ( $2 \times 10^{-4} \Omega \text{ cm}$ ) reported in [18]. However, for seeking high energy density of batteries,

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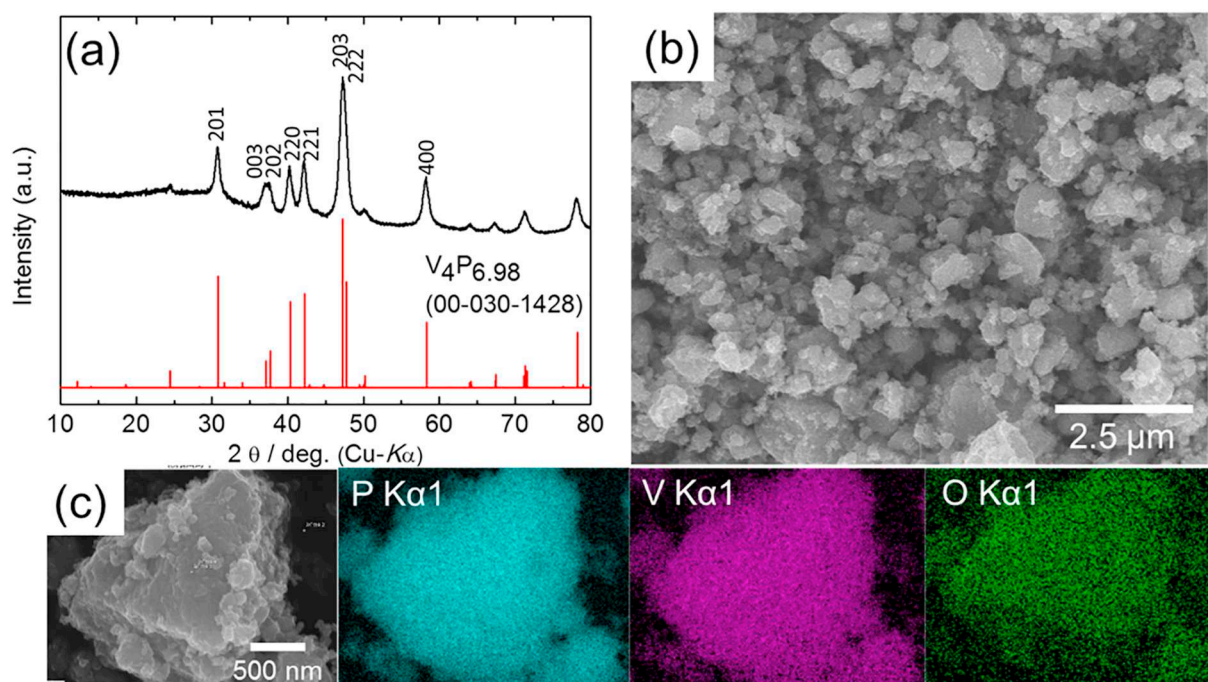


Fig. 1. (a) X-ray diffraction pattern, (b) SEM image, and (c) EDX mapping of  $V_4P_7/5P$  particles.

a higher capacity of negative electrode materials is required. Hence, it will be interesting to investigate  $V_4P_7/P$  composite for the SIBs.

Ionic liquids (ILs) have attracted widespread attention for the safety and high performance aspects owing to the negligible flammability and volatility, wide electrochemical window and high thermal stability [19,20]. Several studies in the past few years have suggested that some negative and positive electrodes exhibit better performance with ILs than with organic electrolytes [21–23]. This is partly explained by the formation of a uniform solid electrolyte interface (SEI) layer in the first cycle and suppression of large volume change in negative electrodes [24]. Another advantage of using ILs is their compatibility with operation at elevated temperatures because of their thermal stability. This is because both the diffusion of  $Na^+$  ions and the electrode reactions are enhanced at elevated temperatures; such a temperature range above room temperature is defined as the intermediate temperature [25,26]. A recent report demonstrated a considerable reduction in the interfacial resistance at intermediate temperatures using ILs [27]. Pyrrolidinium-based binary ILs are known to provide a stable passivation layer, especially in phosphorus-based systems [28,29]. All these observations motivated us to investigate ILs as electrolytes in our study. We have investigated the vanadium phosphide–phosphorus composite,  $V_4P_7/5P$  (and analogues with different V/P ratio), as a negative electrode in SIBs at 298 and 363 K, using the ionic liquid,  $Na[FSA]-[C_3C_1pyrr][FSA]$  (FSA = bis(fluorosulfonyl)amide anion and  $C_3C_1pyrr$  = *N*-methyl-*N*-propylpyrrolidinium cation) IL [30,31], as the electrolyte.

## 2. Experimental

The vanadium phosphide/phosphorus composite,  $V_4P_7/5P$ , was prepared by one-step high-energy ball milling (HEBM) of vanadium metal (Kojundo Chemical Lab, purity 99.9%) and phosphorus powder (Wako Pure Chemical Industries, purity 98%) in a stoichiometric ratio (V:P = 4:12) under Ar atmosphere. The ball to powder ratio was kept at 50:1 at 400 rpm for 20 h. In order to see the effect of the V/P ratio,  $V_4P_7$ ,  $V_4P_7/9P$  (V:P = 4:16), and  $V_4P_7/13P$  (V:P = 4:20) were prepared by HEBM in the same condition. The  $V_4P_7$  without any excess

phosphorus will be called pristine  $V_4P_7$  in this manuscript. Based on the capacity value and capacity retention of the composites,  $V_4P_7/5P$  was chosen as the main material for investigation (Fig. S1). The XRD patterns of the samples were obtained on a Rigaku SmartLab diffractometer (Cu  $K\alpha$  (1.5418 Å), 40 kV – 30 mA). Particle size, morphology, structural parameters, and elemental composition were analyzed by scanning electron microscopy (SEM, Hitachi SU-8020) and scanning transmission electron microscopy (STEM, JEOL JEM-2100F). The chemical bonding states were analyzed by X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9010, Mg $K\alpha$ , 10 kV–10 mA).

The test electrodes were prepared by mixing the active material ( $V_4P_7$ ,  $V_4P_7/5P$ ,  $V_4P_7/9P$ ,  $V_4P_7/13P$ ), acetylene black (Wako Pure Chemical Industries), and a carboxymethyl cellulose/styrene-butadiene binder in a weight ratio of 75:15:5 in water. The resulting slurry was subsequently cast on an Al foil and dried under vacuum, first at 363 K for 10 h and then overnight at 383 K (mass loading:  $\sim 1 \text{ mg cm}^{-2}$ ). The  $Na[FSA]-[C_3C_1pyrr][FSA]$  IL was prepared by mixing the two salts ( $Na[FSA]$ : Mitsubishi Materials Electronic Chemicals Co., Ltd., purity > 99%, and  $[C_3C_1pyrr][FSA]$ : Kanto Chemical Co., Inc., purity > 99.9%), which were first vacuum-dried at 353 K in a 2:8 M ratio and further vacuum-dried at 363 K for > 10 h. A glass fiber filter (Whatman, GF-A, 260 mm in thickness and 16 mm in diameter) was used as a separator, and a sodium metal disc (Aldrich, purity 99.9%) was used as the counter electrode. Electrochemical performance was tested by assembling a 2032 coin cell under Ar atmosphere. For ex situ XRD measurements, the electrodes were taken out of the coin cells in both the charged and discharged states, rinsed with tetrahydrofuran, and vacuum-dried for one day at room temperature. The electrochemical impedance spectroscopy measurements were performed with a VSP potentiostat (Bio-Logic) at 298 and 363 K over a frequency range from 100 mHz to 100 kHz, with an AC amplitude of 20 mV.

## 3. Results and discussion

Fig. 1 (a) shows the XRD pattern of  $V_4P_7/5P$  prepared by HEBM. All the peaks are assigned to tetragonal  $V_4P_7$  (space group  $P-4m2$ ) that

has a partial occupancy of 0.75 for one of the two P sites; [18] however, a slight deviation in the stoichiometry is possible. The XRD pattern suggests the formation of a crystalline  $V_4P_7$  phase with an amorphous red phosphorus phase (5P, considering the stoichiometry in the initial state), although the latter cannot be detected in XRD. On the other hand, the peaks of pristine  $V_4P_7$ ,  $V_4P_7/9P$ , and  $V_4P_7/13P$  are also indexed to  $V_4P_7$  (Fig. S2), suggesting the increase of the P/V ratio simply leads to the increase of the amorphous phosphorus phase. The particle size and morphology were analyzed by SEM (Fig. 1(b)). Continuous collision and fracture during ball-milling resulted in a random morphology of the particles. The size of the particles ranges from 500 nm to a few micrometers. Elemental mapping in the energy-dispersive X-ray (EDX) spectrum suggests that the elements in the  $V_4P_7/5P$  composite were uniformly distributed in the particle (Fig. 1(c)). A small amount of oxygen, as confirmed from the mapping, can be attributed to the oxidation of the elements during ball-milling owing to the high rotational speed of operation. This was further confirmed by the presence of oxide ( $V^{2+}$ ) peaks around 522.1 and 513.6 eV and  $V^{5+}$  peaks (516.7 and 523.2 eV) in the V 2p XPS and at 134 eV in the P 2p XPS owing to  $-PO_4$ -bond in  $VOPO_4$  (Fig. S3(a) and (b)). The peaks in V 2p and P 2p (512.7 and 130.1 eV, respectively) can be indexed to both the existence of elemental vanadium (512.6 eV), phosphorus (130.1 eV), and the formation of  $V_4P_7$  because the binding energies values are very close to each other. Although there is no XPS data for  $V_4P_7$ , its binding energy is considered to be close to that of VP (V 2p = 512.6 and P 2p<sub>3/2</sub> = 129.1 eV, respectively) because the binding energies of the most 3d transition metal phosphides are similar to each other (P 2p<sub>3/2</sub> for FeP, MnP, and TiP are 129.5, 129.4, and 128.4 eV, respectively). [32]

To obtain the composition of  $V_4P_7/5P$  and to confirm the presence of excess elemental phosphorus in the amorphous structure, further characterization is required. Therefore, the high-resolution HRTEM image of the pristine powder was captured (Fig. 2(a)). The *d*-spacing of  $V_4P_7/5P$  was estimated by the fast Fourier transformation (FFT, Fig. 2(b)) of two specific regions. The results confirmed the formation of  $V_4P_7$  nanocrystallites of size 5–15 nm, embedded within the amorphous phosphorus matrix. Elemental mapping of the composite also supports this argument, as the excess phosphorus can be observed around the nanocrystallites of  $V_4P_7$  (Fig. 2(c)). The atomic ratio of P and V, calculated for several particles by STEM-electron energy loss spectroscopy, was in the range 2.3–2.6 (Fig. S4), which is in good agreement with the ratio of the materials used for HEBM.

The electrochemical performance of the  $V_4P_7/5P$  composite with IL as the electrolyte is shown in Fig. 3. Fig. 3(a) and (b) represents the galvanostatic charge–discharge curves at 298 and 363 K, respectively, for the first three cycles at 100 mA g<sup>−1</sup> in the voltage range 0.005–2 V. The curves at 298 K for the charging process (Fig. 3(a)) of the first cycle consists of a sloping profile with one indistinct plateau around 0.15 V. A high first-cycle coulombic efficiency of 88% indicates that the side reactions in the first cycle are highly suppressed in this electrode in an IL, in contrast to that reported for other negative electrodes such as hard carbon and phosphides, wherein the efficiency was typically lower than 75% [8,33]. During desodiation, all the curves for the first three cycles overlap with each other, which indicates a reversible extraction of sodium from the composite matrix. The curves obtained at 363 K (Fig. 3(b)) are indicative of lesser polarization and contains more plateaus owing to the increase in temperature. The plateau at 0.25 V is more distinct than that at 298 K for the same voltage. Details on plateau potentials are further discussed by cyclic voltammetry (Fig. S5). At 100 mA g<sup>−1</sup>, the high first-cycle discharge capacities at 298 and 363 K were 560 and 738 mAh g<sup>−1</sup>, respectively, while the coulombic efficiencies at 298 and 363 K were 88% and 86%, respectively. In the rate capability test at 363 K (Fig. 3(c)), this system exhibited high discharge capacities of 695, 537, and 360 mAh g<sup>−1</sup> at the rates of 100, 1000, and 8000 mA g<sup>−1</sup>, respectively. Even at 298 K, reasonable discharge

capacities of 588, 271, and 155 mAh g<sup>−1</sup> were observed at the rates of 100, 1000, and 2000 mA g<sup>−1</sup> respectively. Fig. 3(d) shows the cycle performance (the first two cycles were performed at 100 mA g<sup>−1</sup>) for 100 cycles at 298 K (rate = 200 mA g<sup>−1</sup>) and 363 K (rate = 500 mA g<sup>−1</sup>). In the fourth cycle, the discharge capacities at 298 and 363 K were 548 and 613 mAh g<sup>−1</sup>, respectively, while the coulombic efficiencies at the same temperatures were 99.2% and 99.3%, respectively. The capacity increased for the first 20 cycles at 298 K owing to the activation and then gradually decreased. Cyclability test at 363 K indicated a constant capacity for few cycles, followed by a decrease in the capacity. This was similar to that observed at 298 K. After 100 cycles, the capacity retention reached 54% and 48% at 298 and 363 K, respectively, with corresponding coulombic efficiencies of 98.1% and 99.1%. The cyclability was also evaluated at 298 K using 1 M NaPF<sub>6</sub> in an organic electrolyte, ethylene carbonate/diethylene carbonate (1:1 (v/v)), in order to compare the performance with that in the IL electrolyte. The first charge–discharge curves at the rate of 100 mA g<sup>−1</sup> (cut-off voltage range 0.005–2 V) delivered a discharge capacity of 605 mAh g<sup>−1</sup>, with a coulombic efficiency as high as 88% (Fig. S6(a)). Although the reaction was reversible till the fifth cycle, severe capacity degradation could be observed after that (Fig. S6(b)). A similar behavior was also reported for Sn<sub>4</sub>P<sub>3</sub> and phosphorous negative electrodes [28], wherein the SEI layer was found to be non-uniform in the organic electrolyte. Na[FSA]-[C<sub>3</sub>C<sub>1</sub>pyrr][FSA], however, provided a uniform passivation layer.

The electrochemical performance of the pristine  $V_4P_7$  was measured at 298 and 363 K for comparison (Fig. S7(a) and Fig. S1(a)) shows the charge–discharge curves at 100 mA g<sup>−1</sup> for the first three cycles at 298 and 363 K, respectively. The obtained reversible discharge capacity at 298 K with IL is 270 mAh g<sup>−1</sup> (~1 Na<sup>+</sup> per VP<sub>1.75</sub> unit) which is similar to the reported value in [17] but when the temperature is raised to 363 K, the discharge capacity for first cycle reaches 470 mAh g<sup>−1</sup> (1.85 Na<sup>+</sup> per VP<sub>1.75</sub> unit) with the initial coulombic efficiency of 71%. Although the pristine  $V_4P_7$  exhibits a high cyclability,  $V_4P_7/5P$  has an advantage in capacity. Increase of phosphorus content in the composite ( $V_4P_7/9P$ , and  $V_4P_7/13P$ ) increases the first cycle capacity at the cost of severe capacity fading. By considering these data,  $V_4P_7/5P$  is regarded as a well-balanced material in this series in terms of capacity and cyclability.

The charge–discharge mechanism was analyzed by ex situ XRD (Fig. 4). The rate of charging and discharging was 100 mA g<sup>−1</sup>, in the cut-off voltage range 0.005–2 V. The XRD pattern of the pristine sample shows peaks corresponding to  $V_4P_7$ . There is no difference between the XRD patterns of the pristine sample and the one charged at 0.24 V. Peaks for Na<sub>3</sub>P could be observed after charging to 0.005 V, although the peaks corresponding to  $V_4P_7$  remained intact. This result is similar to the previous report which observed no change in the peaks of  $V_4P_7$  [17]. Na<sub>3</sub>P was desodiated during discharging, as evident from the decrease in the number and intensities of the XRD peaks of Na<sub>3</sub>P at 0.54 V. The peaks ultimately disappeared at 2 V. The XRD patterns in the second cycle indicates the reversibility of the reaction. Moreover, the ex-situ XRD of the pristine  $V_4P_7$  also supports the arguments above as there is no change in the peaks for charged and discharged samples (Fig. S8).

To see the change in resistance with cycling in different electrolytes, impedance spectra of  $V_4P_7/5P$  were measured in a half cell configuration with IL (298 and 363 K) and organic electrolytes at 298 K (Fig. S9(a), (b) (inset: magnified plot) and (c)), respectively. The  $V_4P_7/5P$  electrode was charged and discharged for one, three, and ten cycles, and then charged to 0.5 V during the next charging step. A constant decrease in the interfacial resistance till the tenth cycle is observed in IL at both 298 and 363 K, though the initial value for IL at 298 K is larger than that for organic electrolyte owing to the development of surface film between sodium metal and IL electrolyte, [27] while the interfacial



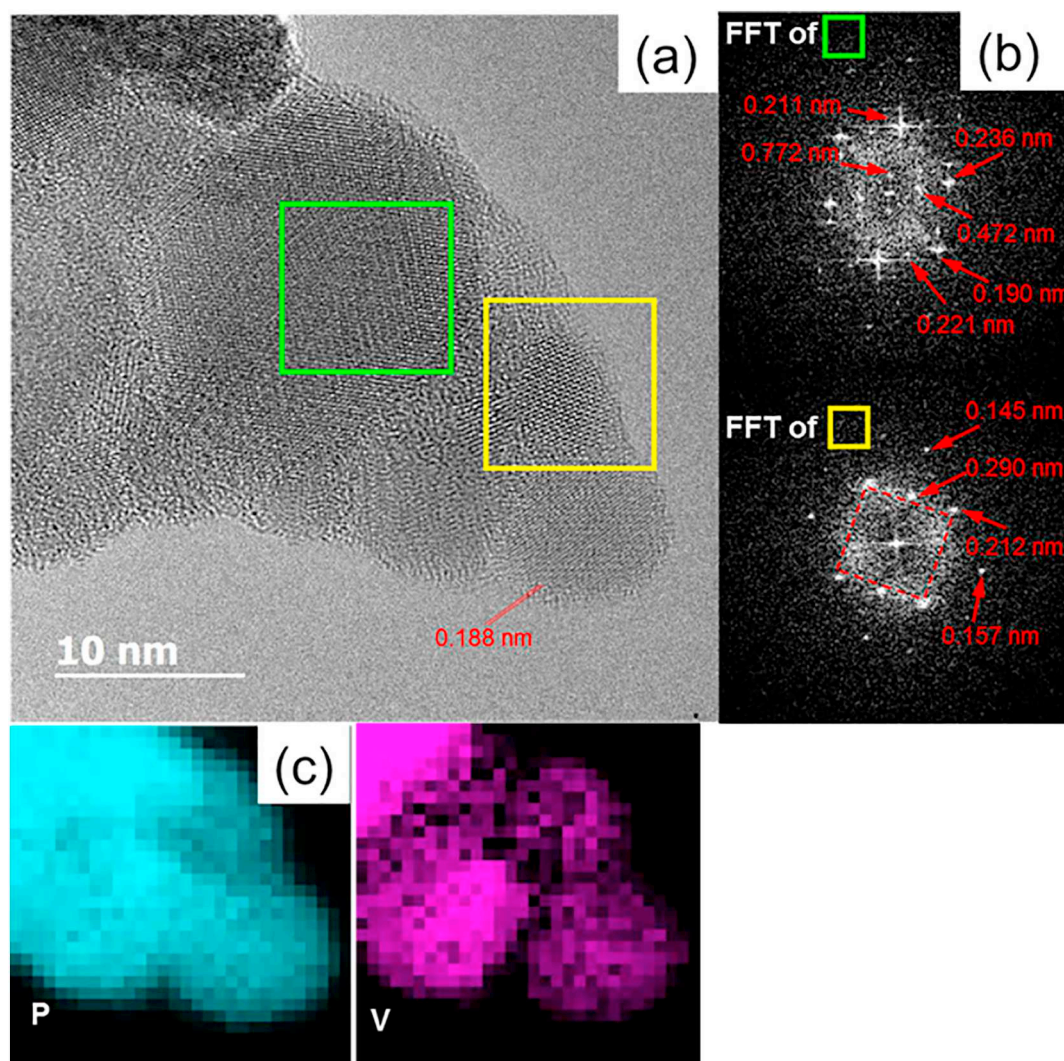


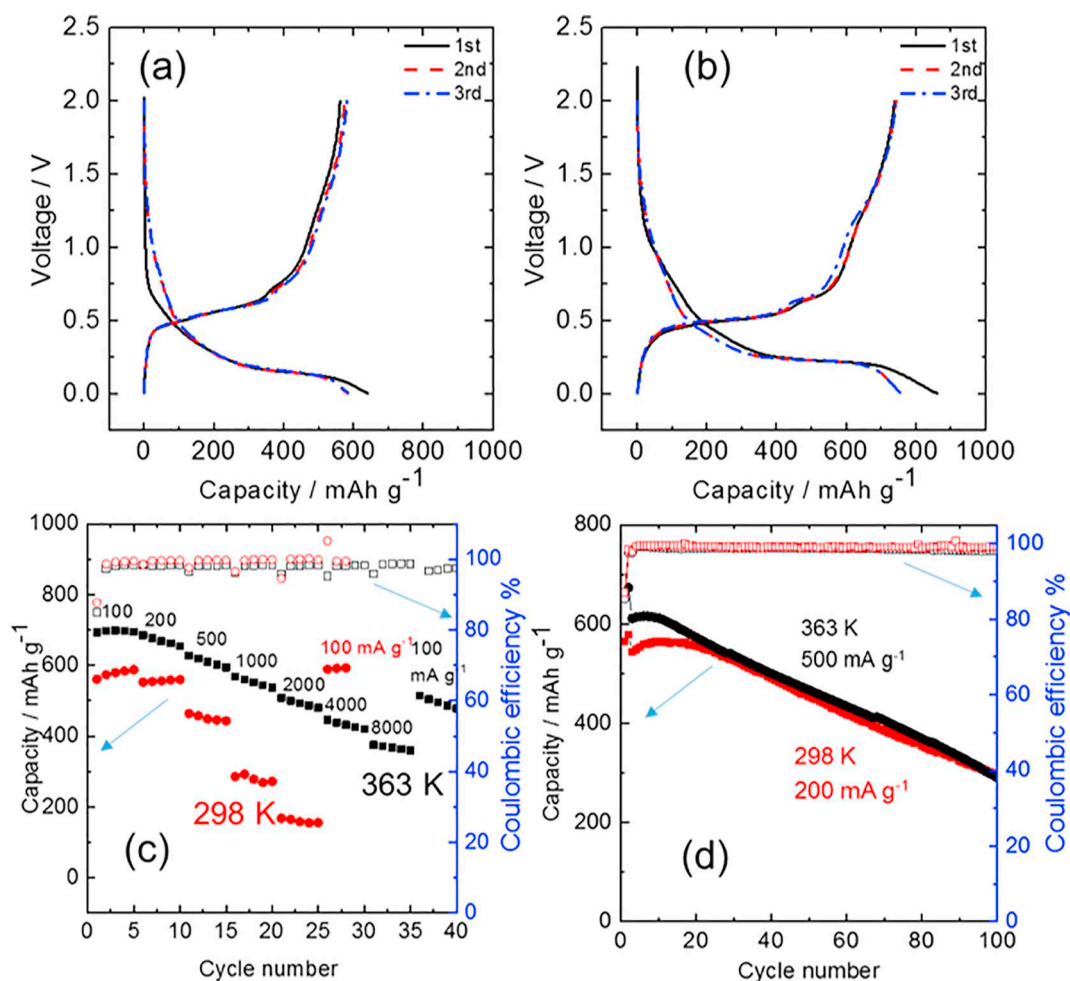
Fig. 2. (a) HRTEM of the  $V_4P_7/5P$  particles, (b) FFT of the particles in the two areas marked in (a), and (c) elemental mapping of the particles.

resistance increases drastically after the first cycle in the organic electrolyte. This correlates with the cyclability test, confirming the benefit of IL over organic electrolytes with respect to the performance. This result is further supported by the surface analysis of electrode after 10 cycles in IL and organic electrolyte by SEM (Fig. S10(b) and (c), respectively). Substantial increase in particle size is clearly evident in the case of organic electrolyte whereas, it is almost the same as pristine (Fig. S10(a)) in IL electrolyte. Similar results were obtained in case of silicon negative electrode in LIBs [24].

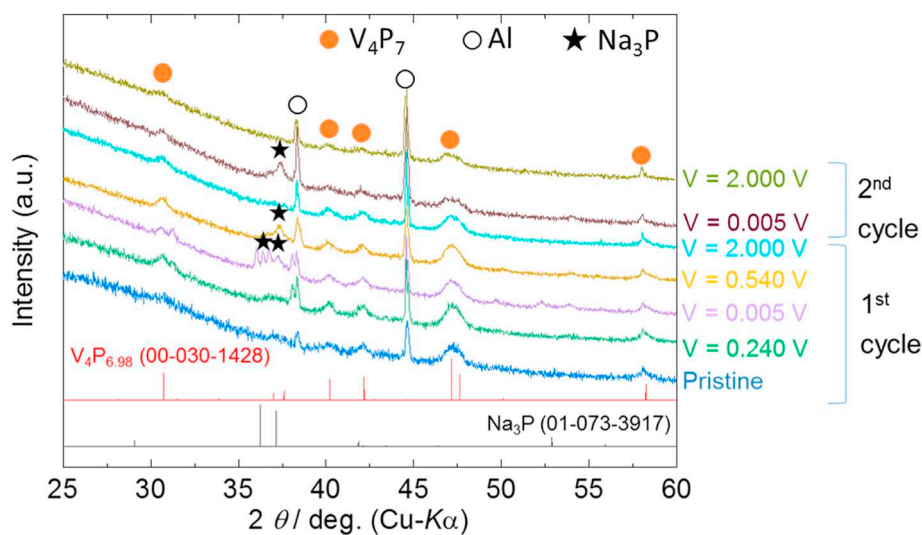
The enthalpy of formation [34] and reaction mechanism for some selected 3d transition metal phosphides ( $MP_x$  with low  $x$  value) used in LIBs and SIBs are summarized in Table S1. The enthalpy of formation of  $MP_x$  (per mole of the respective transition metals) increases with increasing atomic number, and titanium and vanadium phosphides have significantly small (large negative) enthalpies of formation. This prevents the conversion reaction of these phosphides with high lattice energy in both LIBs and SIBs, and it was certainly reported that  $V_4P_7$  works based on the topotactic insertion mechanism. All the late 3d transition metal phosphides are active for the conversion reaction because of their low negative enthalpies of formation. Further discussion from the viewpoint of thermodynamics is difficult here because of the lack of reliable data.

#### 4. Conclusions

In this study, we reported for the first time the use of a  $V_4P_7/5P$  composite as a negative electrode for SIBs, using an IL as the electrolyte. The XRD, HRTEM, SEM, and XPS analyses confirmed the formation of  $V_4P_7/5P$  and revealed the morphology and particle size. Large reversible capacities of  $560 \text{ mAh g}^{-1}$ , with a large coulombic efficiency of 88%, and  $738 \text{ mAh g}^{-1}$ , with a coulombic efficiency of 86%, were observed at 298 and 363 K, respectively, in the absence of carbon materials. A capacity of  $360 \text{ mAh g}^{-1}$  was obtained even at a high rate of  $8000 \text{ mA g}^{-1}$  at 363 K, and 47.2% capacity retention was achieved after 100 cycles. The ex situ XRD analysis revealed the reversible sodiation and desodiation of phosphorus in  $Na_3P$  and the insertion mechanism of  $V_4P_7$  phase. The advantage of  $V_4P_7$  is to provide mechanical integrity, electrical conductivity and capacity to the electrode for better performance. Moreover, the interfacial layer in IL was better than that in the organic electrolyte. Our results demonstrated a good performance and safer operation by utilizing metal phosphide and IL in SIBs. The results of this study can certainly be extended to the practical applications of large-scale SIBs, without the use of rare elements.



**Fig. 3.** Galvanostatic charge-discharge curves of the  $V_4P_7/5P$  composite electrode in IL electrolyte (half-cell configuration) at (a) 298 K and (b) 363 K (rate:  $100 \text{ mA g}^{-1}$ , voltage range: 0.005–2.000 V), (c) rate capability at 298 K and 363 K (rate: 100–8000  $\text{mA g}^{-1}$ ), and (d) cyclability at 298 K (rate:  $200 \text{ mA g}^{-1}$ ) and 363 K (rate:  $500 \text{ mA g}^{-1}$ ) for the first two cycles at  $100 \text{ mA g}^{-1}$ .



**Fig. 4.** Ex situ XRD patterns of the  $V_4P_7/5P$  composite obtained with IL electrolyte for the first cycle (charging: pristine, 0.24 V, 0.005 V and discharging: 0.54 V and 2 V) and second cycle (0.005 V and 2 V).

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2019.03.014>.

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